PB-215 134

A STUDY OF THE DETERMINATION OF PHENOL AND STRUCTURALLY RELATED COMPOUNDS BY THE GIBBS METHOD

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Public Health Service
Cincinnati, Ohio

January 1947

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Cincinnati, Ohio

January, 1947

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A Study of the Determination of Phenol and Structurally Related Compounds by the Gibbs Method

Preliminary to the study of the persistence of phenolic materials in surface water, methods for the determination of phenol and certain closely allied materials have been re-examined. The techniques finally selected differ from those currently used and offer definite advantages where quantitative results are required. Because of these advantages, the modified methods as worked out in this laboratory are being presented.

For the investigation of problems involving phenolic materials in their relation to water supplies, analytical methods should, if possible, meet certain requirements. (1) They should be sensitive to a few parts per billion of phenol or the cresols. (2) The precision of the method should be as high as can be obtained without sacrifice of sensitivity. (3) Minimal manipulation is desirable. (4) Results should be available as quickly as possible to permit operational adjustments in water plants, etc.

The fundamental studies of Gibbs[1][2] are responsible for the development and understanding of the use of 2,6-dibromquinonechlorimide for the determination of phenolic materials. The phenolic material is reacted with Gibbs reagent in a buffered alkaline solution to produce dyes belonging to the indigo family. The dyes are generally oxidation reduction indicators.[3] They are likely to be blue, green or purple in the alkaline form, the acid form usually being red or orange. After being produced by the Gibbs reaction, they may be extracted with iso-butyl alcohol, n-butyl alcohol, or amyl alcohol[4] to give the dye in the alkaline form, or ethyl acetate will extract the dye in the acid form. As will be shown later, there is a shift in the light absorption characteristics when the dye is extracted with one of the alcohols which extract the alkaline form.

While Gibbs did not give a specific procedure in the basic work,[1] he carried out his reactions in buffered solutions and followed the light transmission of the solutions at the wave length of maximum absorption until maximum color was developed. Gibbs reported further that pH and temperature affected the rate of color formation, and close study of Gibbs' papers leads to the belief that the stability of the color formed is also affected by the same variables. pH values of 9.1 to 9.5 were recommended, and the sensitivity was described as being such that 50 p.p.b. could be detected. The test was quickly adapted to use in water plant practice

by Baylis[5] and Theriault.[6] Both investigators recommended distillation from acid solution, treatment of the distillate with Gibbs reagent under conditions of controlled pH and comparison with standards set up concurrently, and of the same pH as the sample. Baylis used pH values of 9.6 to 10.0, while Theriault recommended a pH of 9.4.

In either procedure, in order to secure the desired sensitivity it is necessary to effect some concentration. Baylis used fractional distillation under closely controlled conditions, while Theriault recommended concentration by alkaline evaporation.

Fractional distillation is not a very satisfactory procedure for routine laboratory work. The number of concentrations of phenol which can be produced in one distillation is quite limited. Further, since phenolic materials are frequently encountered in combination rather than as phenol alone, there is small likelihood that the fractionation of a sample containing a mixture of phenol and ortho and meta cresols would be predictable on the basis of fractionation figures for solutions containing phenol alone. It is apparent, therefore, that procedures including fractional distillation cannot be very satisfactory.

While there would appear to be unlimited opportunity for concentration by alkaline evaporation, in practice it has been found that with some river waters there is a progressive loss of phenol in the alkaline concentration process with subsequent failure to measure the phenol originally present.[7] Hence it would appear that concentration by alkaline evaporation also cannot be used as a means of quantitatively increasing the phenol content in a preliminary process.

Renzoni[8] proposed a procedure based on a series of operations, all successively concentrating the phenol content of a sample, and this procedure is perhaps the only method yet proposed which should be sufficiently sensitive to adequately detect 1 p.p.b. of phenol, the limit set by the drinking water standards.[9] Renzoni's procedure consists of: (a) alkaline evaporation and concentration, (b) acidification followed by ether extraction of the phenolic materials, (c) extraction of the phenol from the ether with caustic soda solution, (d) adjustment of the pH of the caustic extract and carrying out the Gibbs reaction, (f) the dye formed in the Gibbs reaction is extracted with n-butyl alcohol. In all, the procedure as described has a potential increase of the sensitivity of the basic Gibbs reaction of

about 400 times providing no phenol is lost in the concentration. With regard to Renzoni's procedure, which was devised (with a modification) to work on relatively pure samples, containing sulfides, it is necessary to point out that losses of phenol can occur in alkaline concentration, and that the additional purification of the acid distillation may sometimes be needed.

Houghton and Pelly(10) produced indo phenol dyes by the reaction of p-dimethylphenylenediamine with phenolic materials and sodium hypochlorite in bicarbonate buffered solutions, the dye so formed being extracted with chloroform. This procedure appears more complicated than the use of the Gibbs reaction and for this reason has not been investigated further.

The use of the Gibbs reaction, followed by the extraction of the color produced with n-butyl alcohol to further increase the sensitivity of the Gibbs reaction, appeared to be the most promising simple procedure for the determination of phenol. Starting from this point, the determination of phenol, o-cresol and m-cresol using the Gibbs reaction with closely controlled pH, followed by extraction with n-butyl alcohol, was given further study and a procedure adapted to instrumental use was developed.

Sources and Preparation of Chemicals Used

For the work reported, no extreme effort has been made to secure highly purified chemicals. Below is given a list of sources of chemicals used and the purification processes applied:

(1) Phenol - Mercks Reagent grade.

(2) O-cresol - prepared by redistilling Coleman Bell's "Pure" and taking the middle third of the distillate.

(3) M-cresol - prepared by the action of phosphorous pentoxide on thymol and redistilling three times taking the middle fraction only.

(4) P-cresol - prepared by distillation from Eastman's p-cresol, taking the middle fraction. Phenolic impurities, by Gibbs reagent, as o-cresol 1.31 per cent.

(5) O-chlorphenol, p-chlorphenol - laboratory repurified chemicals furnished through the courtesy of Dow Chemical Co.

(6) 1-naphthol - Eastman 170.

Initial Procedure Studies

As a basis for experimentation and study of reactions, the procedure described below was adopted after some preliminary observations.

Reagents and Solutions Required

(1) Borate buffer (Theriault)[6]
3.1 g boric acid ($H BO_3$)
3.5 g K Cl
32. ml of 1.N NaOH

Make up to 1 liter. Make up 5 ml of the above buffer solution to 100 ml with distilled water, and if the pH is not 9.4, add further caustic solution until 5 ml of the buffer solution produces a pH of 9.4 when made up to 100 ml with distilled water.

(2) Gibbs reagent: (alcoholic concentrate) dissolve ~~0.5~~ 0.2 g 2,6-dibromquinonechlorimide in 50 ml of ethyl alcohol. Filter out any residue. This reagent should be used immediately, but, if refrigerated, it may be used for periods up to 1 week.

(3) Gibbs reagent (aqueous dilute solution). Dilute 5 ml of the alcoholic concentrate to 100 ml, use within 30 minutes and preferably immediately.

Procedure

To a solution of the phenolic material being investigated in 300 ml of distilled water add 15 ml of borate buffer. Mix well. Add 4½ ml of the dilute Gibbs reagent. Mix thoroughly immediately after addition of this reagent. Allow to stand from 18 to 24 hours. Add 75 ml of n-butyl alcohol; shake well. Separate the alcohol layer in a 500 ml separatory funnel. Filter to clarify. The alcohol has a more or less permanent turbidity unless filtered, presumably due to an air emulsion. Make the filtrate up to 60 ml.

The color developed may be compared instrumentally. In our work we have used a B. & L. visual spectrophotometer for most of the observations, but similar results have been obtained using a Beckman spectrophotometer.

In either instrument the color of the extract may be compared with a "zero control" or an n-butyl alcohol blank with suitable mathematical correction for the color of the "zero control." By a "zero control" is meant a 300 cc portion of distilled water, treated with reagents and extracted exactly as if with it were a standard or a sample. This correction is necessary because the oxidized indicator has a small but definite absorption of color at the wave lengths used for the phenolic materials studied.

Light Absorption by Products of the Gibbs Reaction

In Figures 1, 2 and 3 are shown light absorption characteristics of the products formed by Gibbs reactions with phenol and o and m-cresol at pH 9.4, and the light absorption characteristics of n-butyl alcohol extracts of these solutions. It will be noted that with these compounds the light absorption characteristics are modified by the extraction, the greatest change taking place in the case of phenol.

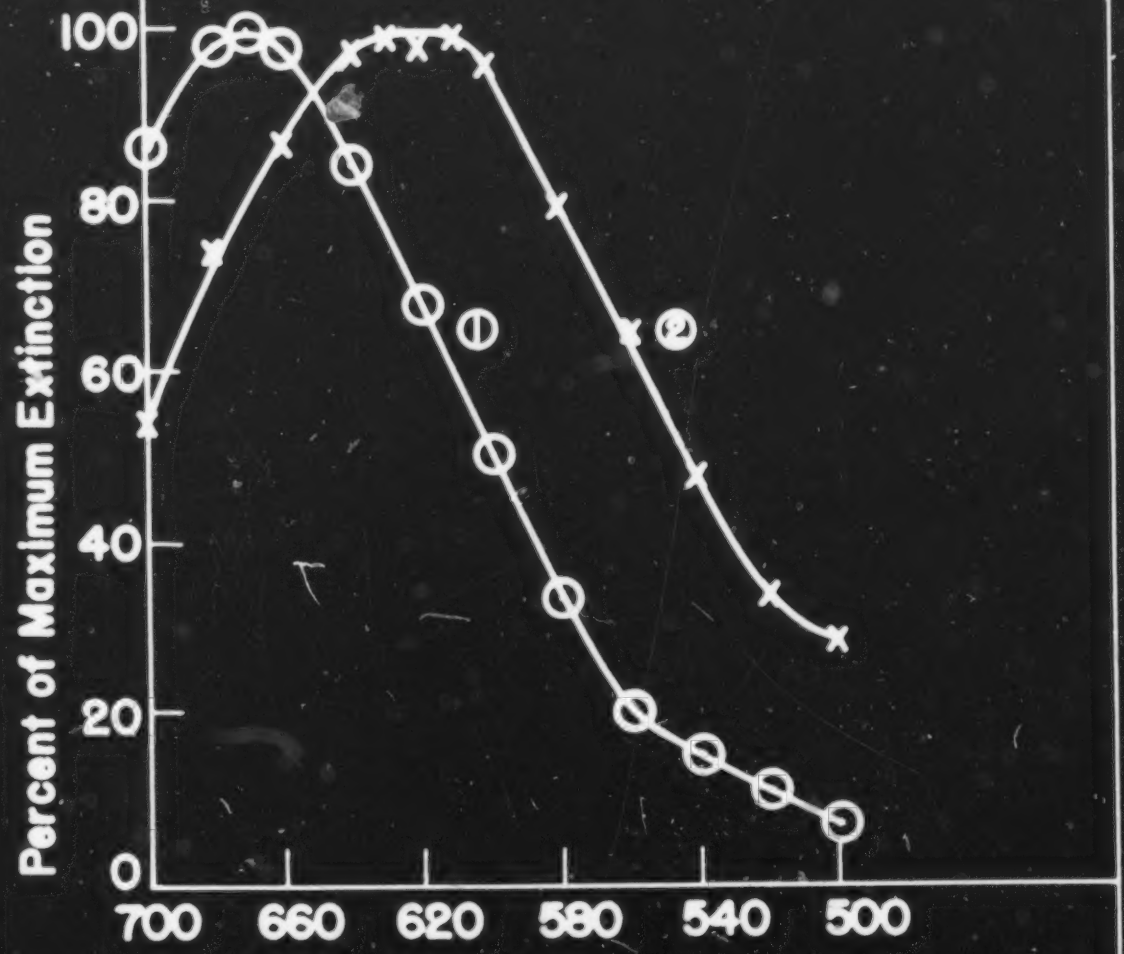
In addition to the displacement of the point of maximum absorption, there is a very definite reshaping of the curve with a sharper peak in the light adsorption curve in some cases. In Table 1 are given the wave lengths of extinction maxima for some phenolic compounds.

Table 1 - Wave Lengths of Maximum Extinction After the Gibbs Reaction at pH 9.4:(1)aqueous, as produced, (2) n-butyl alcohol extract.

Compound	(1) Aqueous	(2) n-butyl alcohol extract
Phenol	610-630	670
o-cresol	600	660
m-cresol	610-620	660-670
1-naphthol	580-600	640
o-chlorphenol	650-670	680-700
p-chlorphenol*	600-620	670

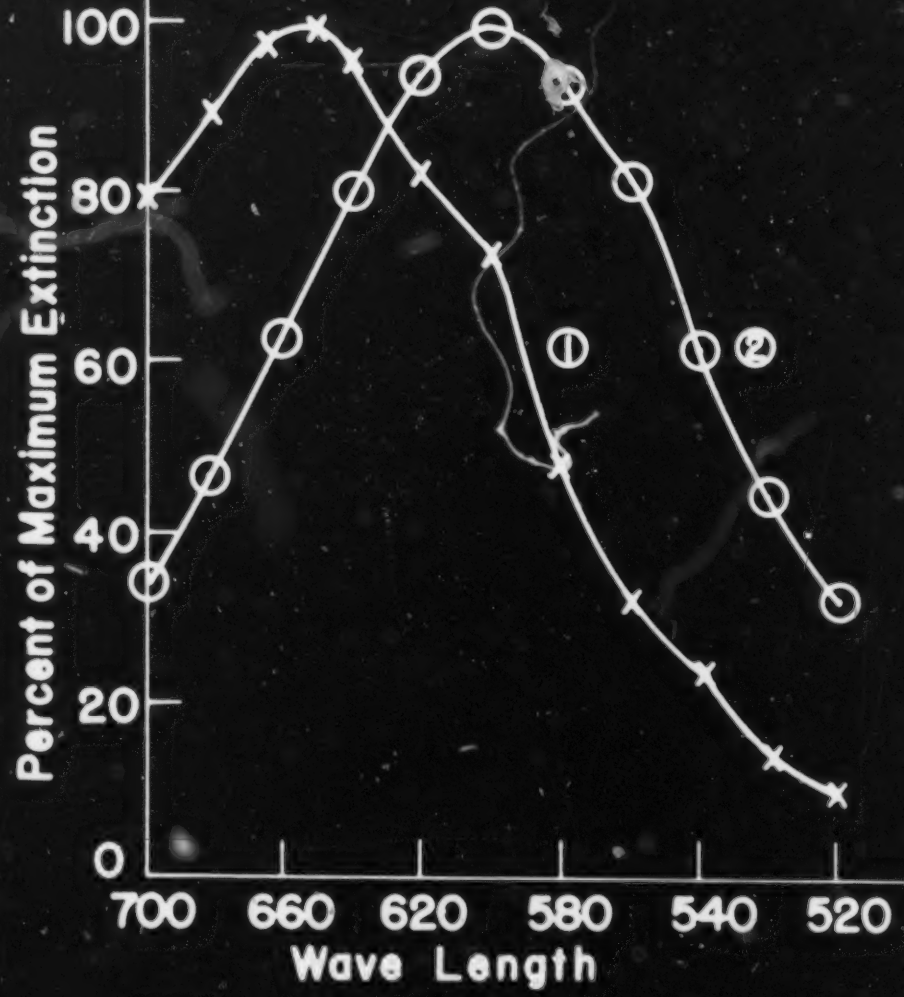
* Presumably yields the same indophenol as phenol. Absorption curves are almost identical.

Fig. 1



Effect of Solvent on Light Absorption Characteristics of Reaction Products of Gibb's Reagent and Phenol
(1) Aqueous Solution as Produced
(2) n-Butyl Alcohol Extract

Fig. 2

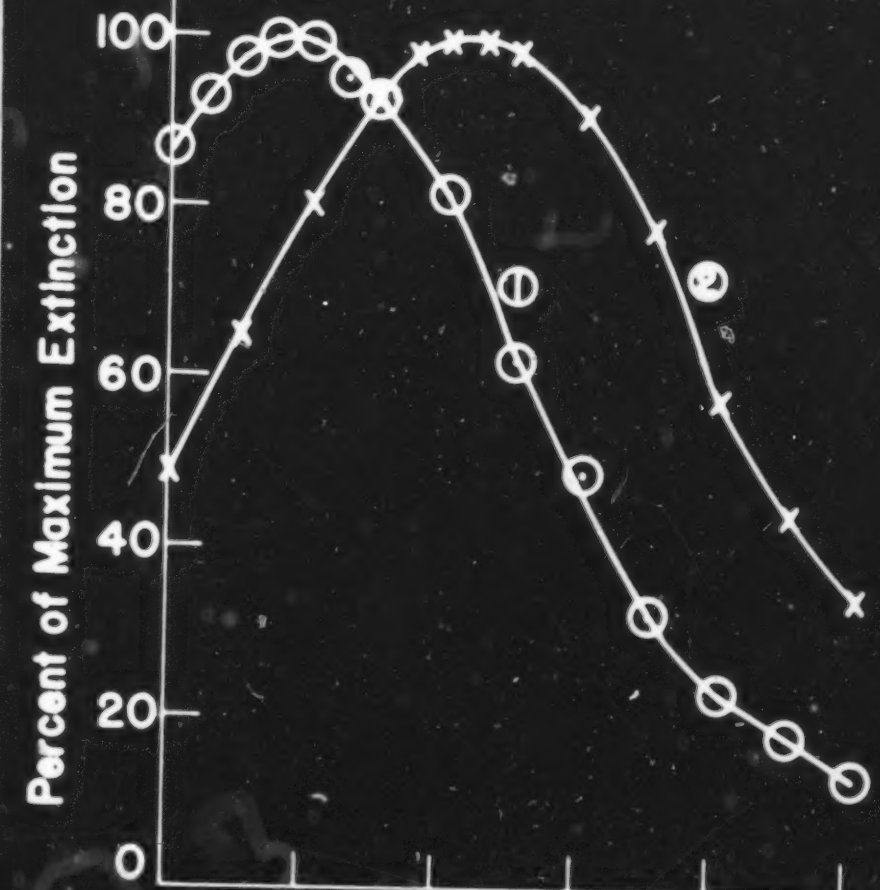


Effect of Solvent on Light Absorption Characteristics of Reaction Products of Gibbs Reagent and O-cresol

(1) Aqueous Solution as Produced

(2) n-Butyl Alcohol Extract

Fig. 3



Effect of Solvent on Light Absorption Characteristics of Reaction Products of Gibbs Reagent and m-cresol

(1) Aqueous Solution as Produced

(2) n-Butyl Alcohol Extract

In Table 2 are given the results of studies made to determine the per cent of the total dye recovered in one extraction by n-butyl alcohol. The results cited or calculated are based on dye recovery by serial extraction with n-butyl alcohol. The volume of the alcohol for the second extraction was chosen so that the n-butyl phase would be the same after both extractions.

In the extractions from the pH 9.4 solutions, the volumetric concentration by the procedure described is only 5.32 to 1. In the case of phenol and o-cresol which have been studied closely, the increase in the extinction coefficients on the basis of the respective aqueous and n-butyl alcohol wave lengths of maximum extinction are respectively: phenol 7.3 times, o-cresol 7.5 times.

Hence it may be seen that, in addition to the volumetric concentration, there is a considerable increase in the amount of light absorption by the dye at the wave length of maximum extinction. Further, the higher color extinction figures at the selected wave lengths do not take into account the incomplete extraction of the dye from the aqueous solution. This relative increase in maximum color extinction is an advantage of the extraction procedure which might not be anticipated.

Laboratory studies have shown that the amount of dye which can be recovered in one extraction may be increased by "salting out" the dye with sodium chloride, and it seems probable that the use of other more soluble salts could result in one-step recoveries of close to 100 per cent of the dye by the solvent. The extraction efficiency could also be increased by serial extractions. However, it was felt that the extra work involved would only result in a slight increase of sensitivity with some sacrifice of precision, and these procedures were not pursued further.

Table 2 - Partition of Color Produced by Gibbs Reagent on Extraction of Reaction Mixture With n-Butyl Alcohol as Described (at Laboratory Temperature).

Compound	Concentration p.p.b.	Extinction coefficient for 15 cm (C) (A) 1st extraction	(B) 2nd extraction	% recovery, 1st extraction	Average* partition coefficient
Phenol	60	1.395	0.34	76.4	
"	100	2.205	.47	78.6	
"	200	3.135	.74	76.4	21.9
O-Cresol	100	1.613	.225	86.0	
"	150	2.375	.33	86.1	
"	200	3.15	.44	86.0	
"	300	4.83	.64	86.7	41.1

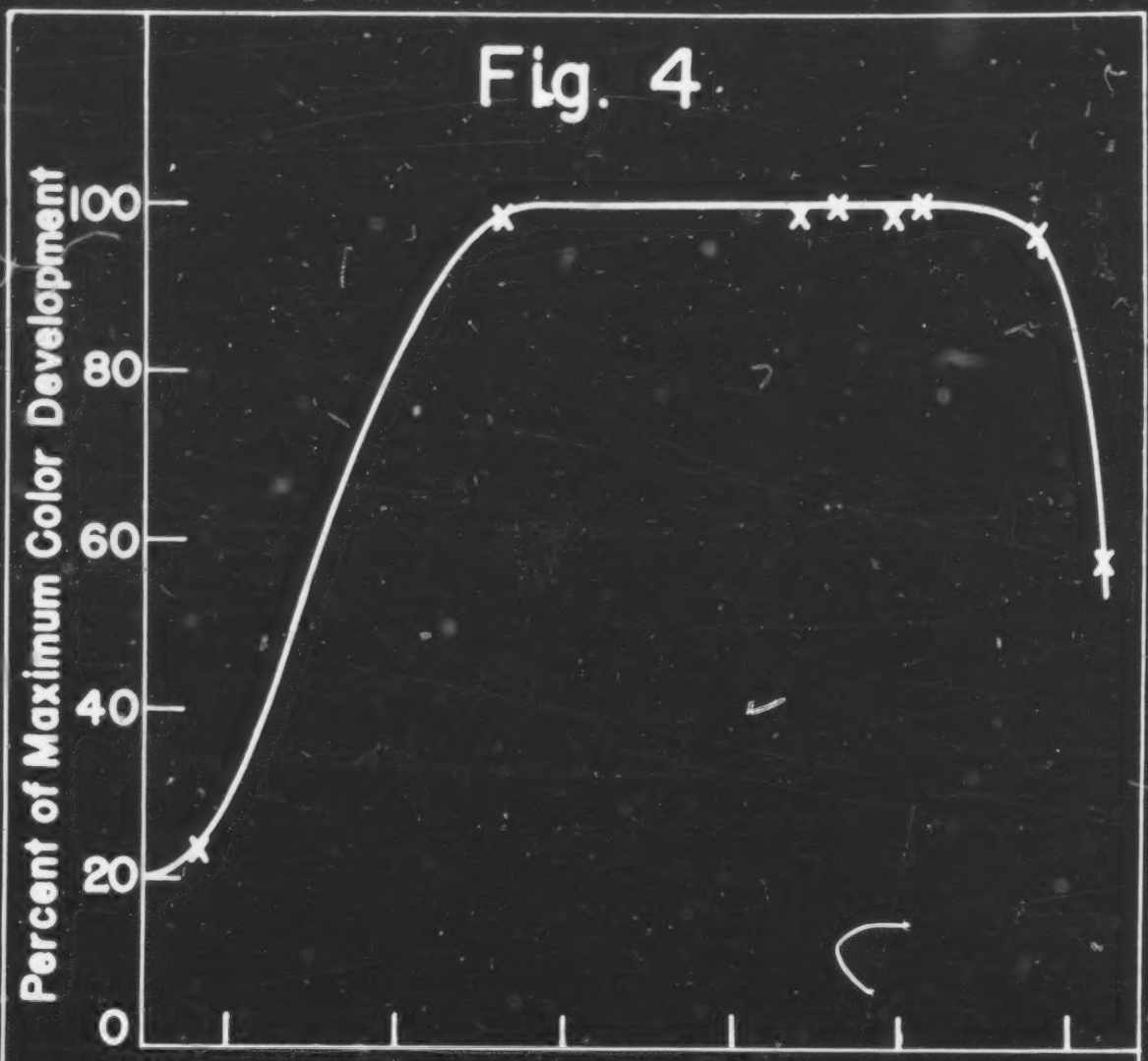
* After the first extraction, 52 cc of n-butyl alcohol phase separated, leaving 342.5 cc of aqueous phase. Second extraction with 52 cc of alcohol. Partition coefficient is for the n-butyl alcohol phase as related to water phase.

(A) Read against a "zero control."
(B) Read against an alcohol blank.
(C) The extract was made up to 60 cc in all cases before optical observations were made.

Effect of pH on the Gibbs Reaction

A fairly wide range of pH values have been recommended as being suitable for carrying out the Gibbs reaction as previously noted. Thus Gibbs advised pH values of 9.1 to 9.5 (9.4 being preferred), Baylis 9.6 to 10.0, and Theriault 9.4. Accordingly, a study of the effect of pH on the color produced and extracted was undertaken to determine how carefully the pH must be controlled and whether or not there is any optimum pH for the reaction. The results of this work are presented in Figure 4, and it may be seen that over a

Fig. 4



Development of Color by 100 ppb of Phenol with Gibbs Reagent at Various pH Values at Laboratory Temperature (25°C±) (Extraction Procedure at 24 hours)

fairly wide range, pH had but little effect on the color developed in 24 hours by 100 p.p.b. of phenol. It should be noted that the buffers used were ordinary borate buffers so that the pH values, based on glass electrode observation, are undoubtedly too high in the range from 9.0 onward due to sodium effect. It seems likely that all the pH ranges or values advocated can be made to work satisfactorily, without ponderable differences in the sensitivity of the reactions.

This set of results is somewhat different from those which might be anticipated on the basis of Gibbs' work[1] since he reported less dye developed at lower pH values (pH 8.5) however, while our results were not repeated, it seems quite apparent that any pH in the range 9.1 to 9.7 should be optimum. On this basis, the pH of 9.4 originally selected was found entirely satisfactory, and seems to have the further advantage that minor deviations in pH control will not affect the results obtained. One of the considerations that undoubtedly concerned Gibbs in his recommendation of the range 9.1 to 9.5 was reaction rate, this pH range being favorable for rapid completion of the Gibbs reaction. Here again the pH value of 9.4 which we have selected seems to qualify adequately. The deviation from Gibbs' findings of our observation is probably caused by differences in quantity of phenol and indicator studied, since Gibbs used larger quantities of phenol and simply added a small amount of solid indicator.

Quantitative Relationships of Reactions

In any analytical reaction it is desirable to have the amount of product for measurement exactly proportional to the amount of the material being determined. When this relationship holds with a colorimetric test, the "density" or extinction coefficient of the color produced is exactly proportional to the amount of material present. In Table 3 are shown the limits under which this linear relationship applies to the determination of some phenolic compounds in so far as we have studied this relationship. As shown by Table 3, the reaction, as we have carried it out, is linear only up to 100 p.p.b. of phenol, and since we have tried to keep our analytical procedures substantially alike for the several materials handled, we have made no attempt to ascertain whether or not the reactionsof other materials were linear in greater concentrations than 100 p.p.b. Procedures simply have been arranged for work with 100 p.p.b. or less of the hydroxy benzene compound under examination.

Table 3 - Linear Relation Between Color and Reaction Products.

Chemical	Limits of linear relation
Phenol	Up to 100 p.p.b.
O-cresol	" " 200 p.p.b. or more
M-cresol	" " 100 p.p.b. and probably much higher
1-naphthol	" " 100 p.p.b. and probably much higher

As a further condition for an analytical reaction, it is desirable to have a constant amount of measurable product produced, by the same amount of active material. Under these conditions with analytical color producing reactions, permanent standards may be prepared or simulated, or a curve set up for a spectrophotometer relating density or per cent transmission with the amount of color produced, making it unnecessary to prepare standards every time a determination is made. Unfortunately this relationship does not hold for the Gibbs reaction.

In Figure 5 are shown the results of three different checks on the relationship of phenol to extinction coefficient. It may be seen that the reaction is linear up to 100 p.p.b. of phenol, but unfortunately there are three different lines. Lines a and b represent much more frequent or normal relationships between the phenol and the amount of dye produced, while line c represents the greatest amount of dye formed per unit of phenol that we have ever encountered. In practical terms, this means that (1) if color standards are used, a new set must be prepared each time a determination is made. However, if a spectrophotometer is used to measure color, only 2 standards are needed - a "zero control" blank and one standard, such as a 100 p.p.b. standard to define the line. In Figure 6 are shown several checks on the linear relationship with ortho and meta cresols. While the two sets of ortho cresol points fall on the same line, this is largely a chance condition, since repeated use of the procedure we have described, with subsequent refinements to be described, has shown a variation in control standards far beyond any differences which could be ascribed to manipulative discrepancies.

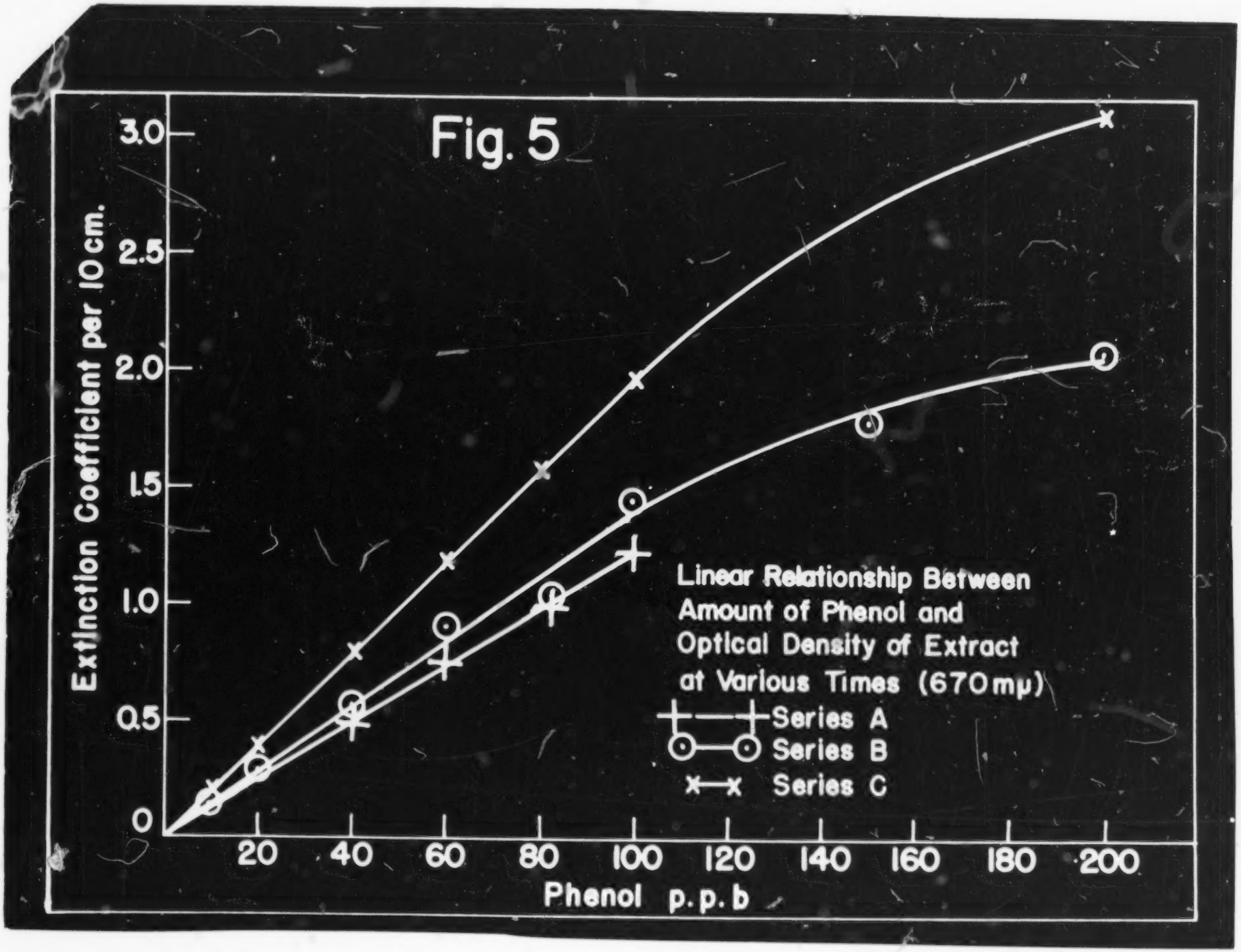


Fig. 5
Extinction Coefficient per 10 cm.
3.0
2.5
2.0
1.5
1.0
0.5
0
20
40
60
80
100
120
140
160
180
200
Phenol p.p.b
Linear Relationship Between
Amount of Phenol and
Optical Density of Extract
at Various Times (670 mμ)
Series A
Series B
Series C

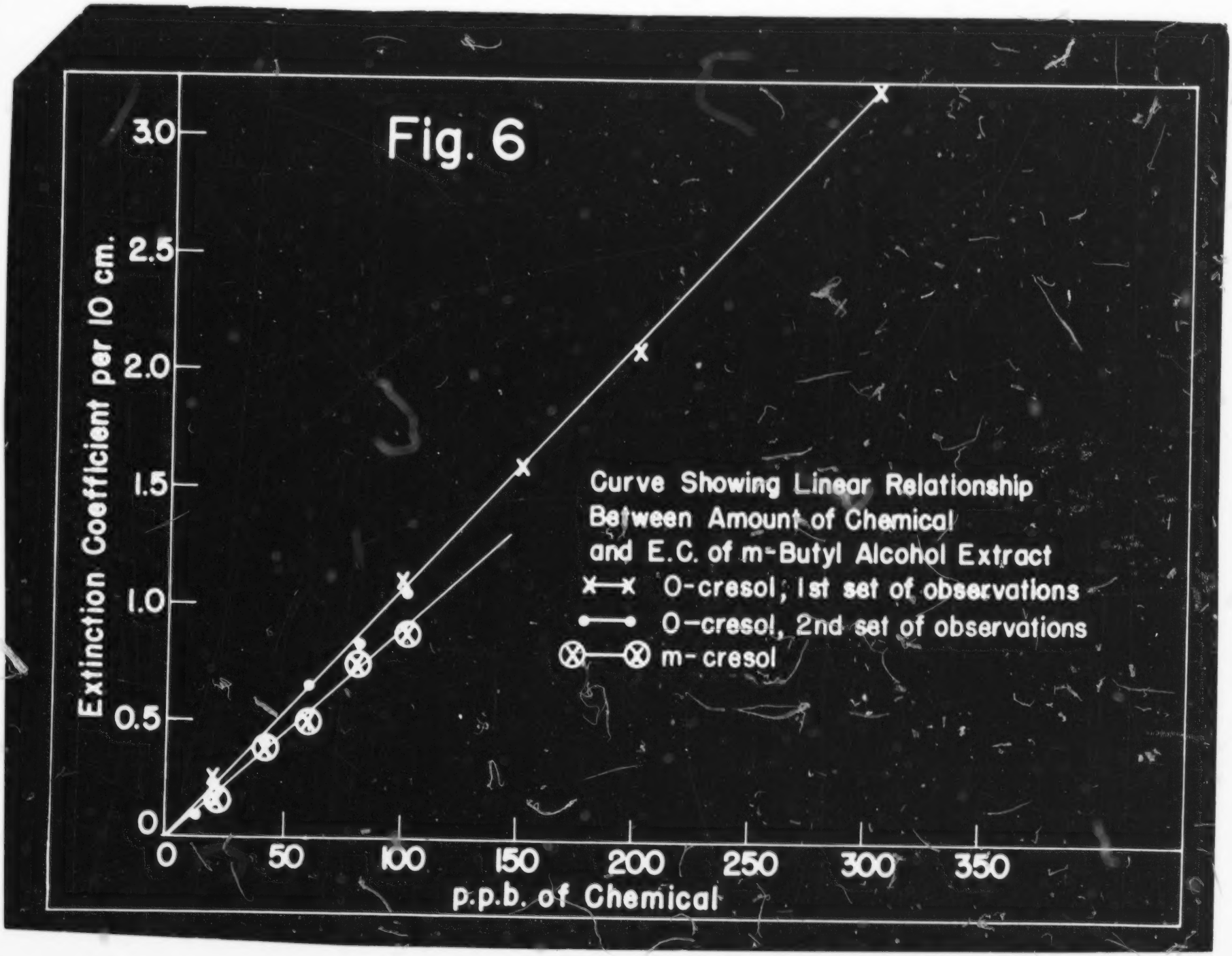


Fig. 6
Extinction Coefficient per 10 cm.
3.0
2.5
2.0
1.5
1.0
0.5
0
0
50
100
150
200
250
300
350
p.p.b. of Chemical
Curve Showing Linear Relationship
Between Amount of Chemical
and E.C. of m-Butyl Alcohol Extract
O-cresol, 1st set of observations
O-cresol, 2nd set of observations
m-cresol

The procedure studied had been rigorously controlled except for three variables, namely: the exact time used for reaction which varied from 16 to 24 hours, the temperature, and the purity and condition of the Gibbs reagent. The 2,6-dibromquinonechlorimide is known to all who have used it extensively as a capricious and unstable reagent which varies from lot to lot, and which must be refrigerated to secure reliable reactions.

In addition to the variability of the reaction caused by the vagaries of the indicator, there is the variation caused by the time and temperature at which the reaction is carried out.

In Table 4 are given the extinction coefficients of a 1000 p.p.b. phenol solution treated with Gibbs reagent at a pH of 9.4. All conditions were maintained as exactly similar as possible, except that the reaction temperatures were different. Figure 8 gives the results of the use of the extraction procedure with 100 p.p.b. of phenol at 20° and 37° respectively. In order to make results strictly comparable in terms of color extraction, the 37° samples were quickly cooled to 20° before extraction.

These data indicate conclusively that the temperature is an important factor in the use of the Gibbs procedure. At ordinary laboratory temperatures, holding periods of from 6 to 24 hours are indicated as satisfactory. If, however, the reaction were carried out at 37°, periods of from 2 to 5 hours' holding are indicated. At the higher temperature, less color is formed per unit of phenol, but the results can be secured much more rapidly. Because of the importance for water plant operators of securing early knowledge of the presence of phenol in the water supply, an alternative procedure, designed for early sensitive detection of phenol, is also suggested later in this paper.

Precision of Observations

Replicate samples containing 100 p.p.b. of phenol, or ortho or meta cresol, were subjected to parallel test using the procedure we have previously described, distillation not being included. Ten samples of each material were so tested. Results of this test are shown in Table 5. It may be seen that the precision of the test as described is adequate for almost any ordinary use. Since the standard deviation of the observation will not be proportionately smaller for smaller amounts of phenolic material, the precision of the method may be expected to decrease somewhat as the amount of the phenolic material decreases.

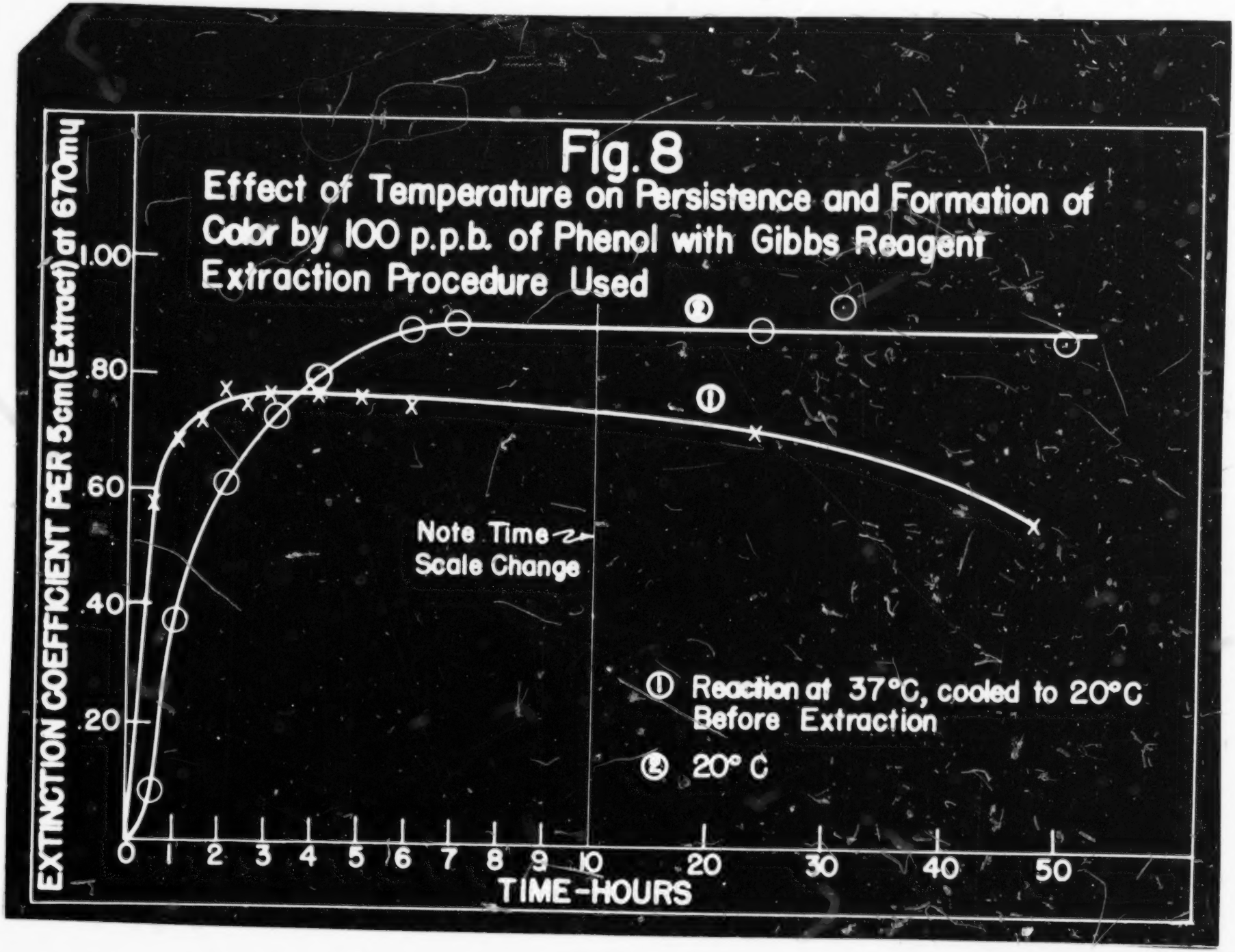


Fig. 8
Effect of Temperature on Persistence and Formation of Color by 100 p.p.b. of Phenol with Gibbs Reagent
Extraction Procedure Used
EXTINCTION COEFFICIENT PER 5cm (Extract) at 670mμ
1.00
.80
.60
.40
.20
Note Time Scale Change
① Reaction at 37°C, cooled to 20°C Before Extraction
② 20° C
0 1 2 3 4 5 6 7 8 9 10 20 30 40 50
TIME-HOURS

Table 4 - Effect of Time and Temperature on the Gibbs Reaction at pH 9.4 - 1000 p.p.b. Aqueous Phenol Treated with Gibbs Reagent at pH 9.4. (Aqueous Solution Examined).

Time after addition of Gibbs reagent (hours)	Extinction coeff. / 10 cm at 610 Mu	
	20°C	37°C
1	0.80	0.71
2	.83	.71
4	.82	.72
6	.80	.71
22½	.80	.71
30	.81	.71
120	.80	.64

Table 5 - Probable Error of Observations Using Extraction Procedure, and 100 p.p.b. of the Material Listed

Material	Phenol	O-cresol	M-cresol
Mean extinction coefficient per 10 cm	1.415	1.020	0.988
Std. dev. of an observation	±0.051	±0.026	±0.035
P.E. of an observation	±0.034	±0.017	±0.023
Per cent P.E. of one observation	±2.3%	±1.7%	±2.3%

Rates of Reaction

In Fig. 7 are shown the rate of production of the dye for 1000 p.p.b. of four phenolic materials. It will be noted that maximum color formation was almost immediate with 1-naphthol, whereas over two hours was required in the case of phenol. These curves do much to clarify the variable results previously noted. Since the 2,6-dibromquinonechlorimide is unstable in aqueous solution, especially if oxygen is present, it seems likely that with those materials which react slowly, the reaction is not complete before the Gibbs reagent has decomposed. As has been previously noted, the reaction is linear for o-cresol up to 300 p.p.b. or more, whereas in the case of phenol it is linear only up to 100 p.p.b. It may be considered quite fortunate that even for quantities of phenol up to only 100 p.p.b. a linear relationship seems to hold under average laboratory conditions. It may be noted further that temperature and the real concentration of active reagent are usually somewhat variable as the reaction is carried out. With both the above factors affecting reaction rates for dye production and the residue of the Gibbs reagent after a given period, the procedure that is described below in detail is necessary for successful use of this reaction for quantitative measurements.

Procedure for Determination of Phenol and o and m Cresols in Surface Waters

Distillation

The distillation is carried out substantially as prescribed on page 246, Section 1-6 of the 1936 edition of Standard Methods.(11)

To a 500 ml sample add 0.7 ml of 10% phosphoric acid. Using an all-glass still, distill over 400 ml at a rapid rate, and 50 ml more slowly. Halt the distillation and add 50 ml of distilled water and distill over a further 50 ml. Thoroughly mix the distillate, and make sure that the temperature is not over 26°C; chill if necessary.

Using an aliquot which will contain from 50 to 100 p.p.b. of the phenolic material under investigation, or 300 cc if the phenolic material totals less than 100 p.p.b., carry out the determination as described earlier under "procedure,"

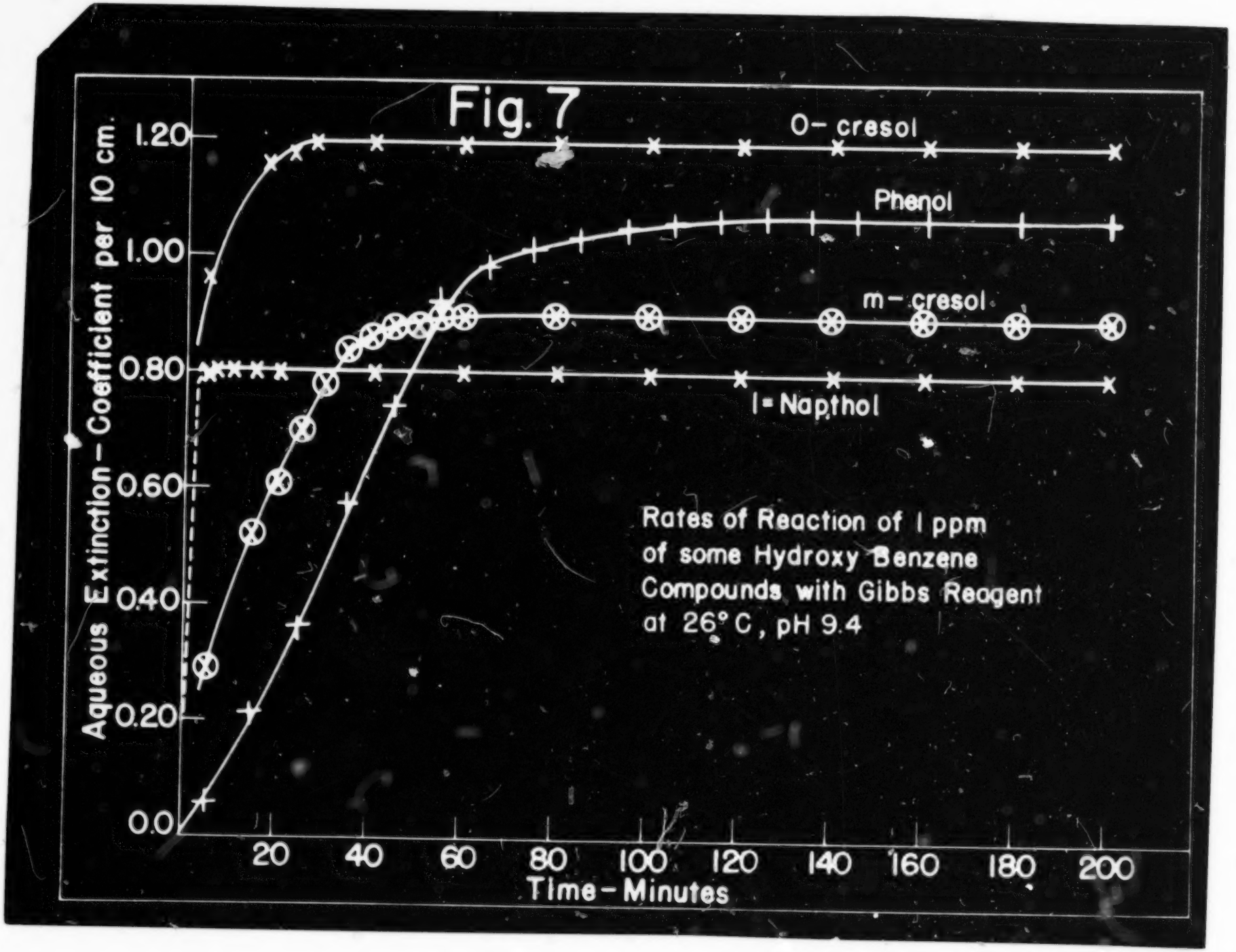


Fig. 7
O- cresol
Phenol
m- cresol
1- Napthol
Rates of Reaction of 1 ppm
of some Hydroxy Benzene
Compounds with Gibbs Reagent
at 26° C, pH 9.4
Aqueous Extinction - Coefficient per 10 cm.
1.20
1.00
0.80
0.60
0.40
0.20
0.0
20
40
60
80
100
120
140
160
180
200
Time - Minutes

subject to the further requirement that the temperature of all sample and control portions shall not vary more than 1°C, plus or minus, at the start of the test, and should preferably be below 26°C. Reaction periods of from 6 to 24 hours may be used.

Photometer Observations

(1) If a known phenolic material is present, determine the extinction coefficient of the extract at the appropriate wave length as indicated in Table 2. Making subtraction allowance for the "zero blank" either by reading the sample against the blank or by calculation. On the basis of the extinction coefficient of a 100 p.p.b. standard the amount of the hydroxybenzene compound present is computed.

(2) If the exact nature of the phenolic material present is not known (This will usually be the case with actual cases of phenolic pollution), the extinction coefficient of the extract is observed at 670 mu and the results reported on the basis of phenol. A phenol standard is used for comparison.

Use of the Procedure for 1-Naphthol

The procedure previously described has been used for 1-naphthol with results which were not too reproducible. Several factors are believed to be responsible.

(1) Aqueous alkaline solutions of 1-naphthol are unstable and make unsatisfactory standards. Neutral alcoholic solutions may be satisfactorily used.

(2) 1-naphthol has a B.P. of 288°C and, with the distillation procedure used, recovery of the chemical in the distillate is believed to be variable and incomplete.

The factors involved in the Gibbs reaction appear to be most favorable for the determination of 1-naphthol, and the authors are of the opinion that a preliminary separation by extraction of acid solution with ether, followed by the extraction of the ether with 1 N NaOH and pH adjustment to 9.4 would give good results.

Sensitivity of Methods Proposed

While the sensitivity of the reactions varies somewhat from time to time as previously noted, the extinction coefficient of the extract from a 100 p.p.b. solution per 10 cm of light path at the wave length of maximum absorption is a rough measure of sensitivity. Given below are relatively frequent values for this parameter.

Chemical	Extinction coefficient of extract from 100 p.p.b. solution, 10 cm light path
Phenol	1.35
O-cresol	1.00
M-cresol	.98
1-naphthol	.44

This indicates a fairly reliable detection of 5 p.p.b. of phenol or the cresols.

Accelerated Method for the Detection of Phenolic Materials

Carry out the reaction exactly as outlined under procedure, subject to the further stipulation that all reaction mixtures are heated to 37°C before the addition of the Gibbs reagent. The mixture is held for one hour in a 37°C incubator or oven.

At the end of the incubation period, the reaction mixtures are cooled to 25°C and extractions, etc., are made as previously described.

This procedure gains time at the expense of accuracy and sensitivity, but should be of use to water plant operators, or it can be easily adapted to serve as a sensitive qualitative method for the detection of phenol.

It should be understood that the above procedures are well adapted to the determination of phenols and o and m cresols in aerobic polluted river waters where the total concentration of these materials may be 1,000 p.p.b. but is more likely to be under 100 p.p.b. Although the principles of these determinations will also apply to the quantitative estimation of these materials in industrial wastes containing much higher concentrations, additional study is

required to determine the procedure best adapted to separation of the phenols in such cases from other interfering organic substances.

Because phenol is frequently the principal phenolic constituent in polluted river waters, it seems undesirable to use standards such as are advised in the ninth edition of Standard Methods[13] which require more than 100 p.p.b. of mixed phenolic material in the standards used, even where simple visual observation is to be used.

Determination of P-cresol

P-cresol does not react with Gibbs reagent, so that another technique must be sought for determination of this material. Only one method has been tried, and the results obtained were at best semiquantitative. The method used is a slight modification of the sulfanilic acid procedure for phenol given by the 1936 edition of Standard Methods.[11] The modification consists in making the observation at 5 minutes rather than after 30 minutes. The usual distillation procedure was used. No attempt has been made to reduce to a sensitive laboratory procedure the more promising use of Millon reagent as described by Gibbs.[12]

Summary and Conclusions

A study of procedures for phenol determination indicated that the use of the Gibbs reaction followed by extraction of the color produced with n-butyl alcohol to increase the sensitivity of the reaction, was the most promising simple procedure for the determination of phenol in aerobic surface waters. It was found that the best results were obtained if the Gibbs reaction was carried out at room temperatures with sample and standard maintained within plus or minus 1.0°C at pH 9.4 for 6 to 24 hours followed by a spectrophotometric examination. The wave lengths for the maximum extinction for the products of the Gibbs reagent with various phenolic materials in both aqueous and n-butyl alcohol solution are given. The maximum adsorption wave length for the Gibbs reagent phenol color, changes from 610-630 mu in aqueous solution to 670 mu in n-butyl alcohol. Similar shifts in maximum adsorption wave lengths were noted from aqueous to n-butyl alcohol solutions for the colored Gibbs reaction products with

other phenolic materials. By the technique used about 76 and 86 per cent of the aqueous color is removed by the first extraction with n-butyl alcohol, from phenol and o-cresol respectively. The color intensification obtained by this extraction based upon increase in extinction at the wave lengths of maximum adsorption is 7.3 and 7.5 times for phenol and ortho cresol respectively. The limits of linear relationship between the Gibbs reaction products and color formed was found to be up to 100 p.p.b. for phenol and at least to 300 p.p.b. for o-cresol. On the basis of these studies a detailed procedure for phenols and cresols in surface waters using spectrophotometric examination at the wave lengths of maximum absorption is proposed. An accelerated procedure for obtaining early information, with concurrent loss of some sensitivity and accuracy, is also offered.

It was shown that on waters containing 100 p.p.b. of the pollutants the recommended procedure was capable of results with a probable error of only plus or minus 2.3, plus or minus 1.7, and plus or minus 2.3 per cent for one observation for phenol, o-cresol and m-cresol respectively.

The authors wish to acknowledge the assistance of Scientific Aide R. J. Liska with the analytical observations in this report.